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Influence of Metal Ion and Polymer Core on the Melt Rheology of Metallosupramolecular Films

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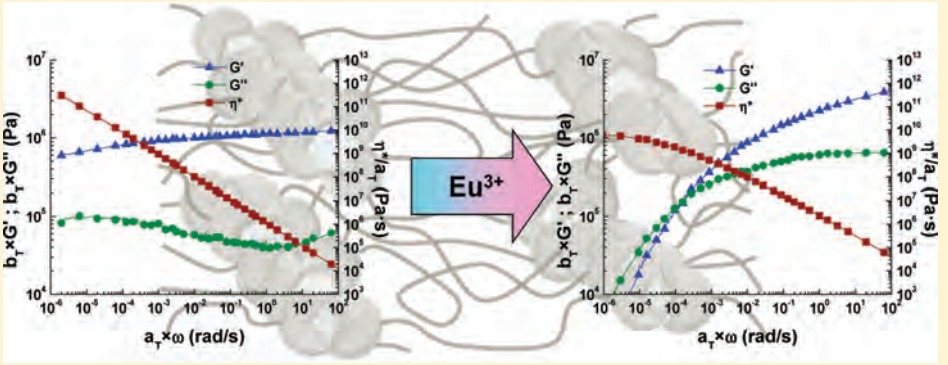
ABSTRACT:



Detailed rheological studies of metallosupramolecular polymer films in the melt were performed to elucidate the influence of the metal ion and polymer components on their mechanical and structural properties. 4-Oxy-2,6-bis(*N*-methylbenzimidazolyl)pyridine telechelic end-capped polymers with a low-T_g core, either poly(tetrahydrofuran) or poly(ethylene-*co*-butylene), were prepared with differing ratios of Zn^{2+} and Eu^{3+} to determine the influence of polymer chain chemistry and metal ion on the properties. Increasing the amount of the weaker binding europium yielded more thermoresponsive films in both systems, and results show that the nature of the polymer core dramatically affected the films mechanical properties. All of the films studied exhibited large relaxation times, and we use this to explain the pure sinusoidal behavior found in the "nonlinear" viscoelastic region. Basically, the system cannot relax during a strain cycle, allowing us to assume the network destruction and creation rates to be only a function of the strain amplitude in a simplified network model used to rationalize the observed behavior.

INTRODUCTION

Supramolecular polymers utilize reversible, noncovalent interactions to achieve high molecular weight materials that combine the properties of typical covalent polymers with those of low molecular weight molecules.[1−6] These polymers have gained increasing interest from a materials' properties standpoint as they can have mechanical properties similar to covalent polymers but have much greater temperature-dependent viscosities as a result of the reversible interactions, which allows easy processing and/or the material to exhibit stimuli-responsive behaviors.[7−11] An additional benefit of these types of polymers is that their properties are widely tailorable simply by modifying the reversible interaction used. A number of noncovalent interactions have been utilized to access such materials, with the largest focus being on hydrogen bonding.[12−15] Another type of interaction that has become popular is metal−ligand coordination[16−20] which allows for a wide range of properties as many different ligands and metal ions can be used. While detailed studies of the melt rheological properties of supramolecular polymers assembled with hydrogen bonds have been carried out,[21−26] the same is not the case for metallosupramolecular polymers. In-depth solution rheological studies of metal-coordination polymers

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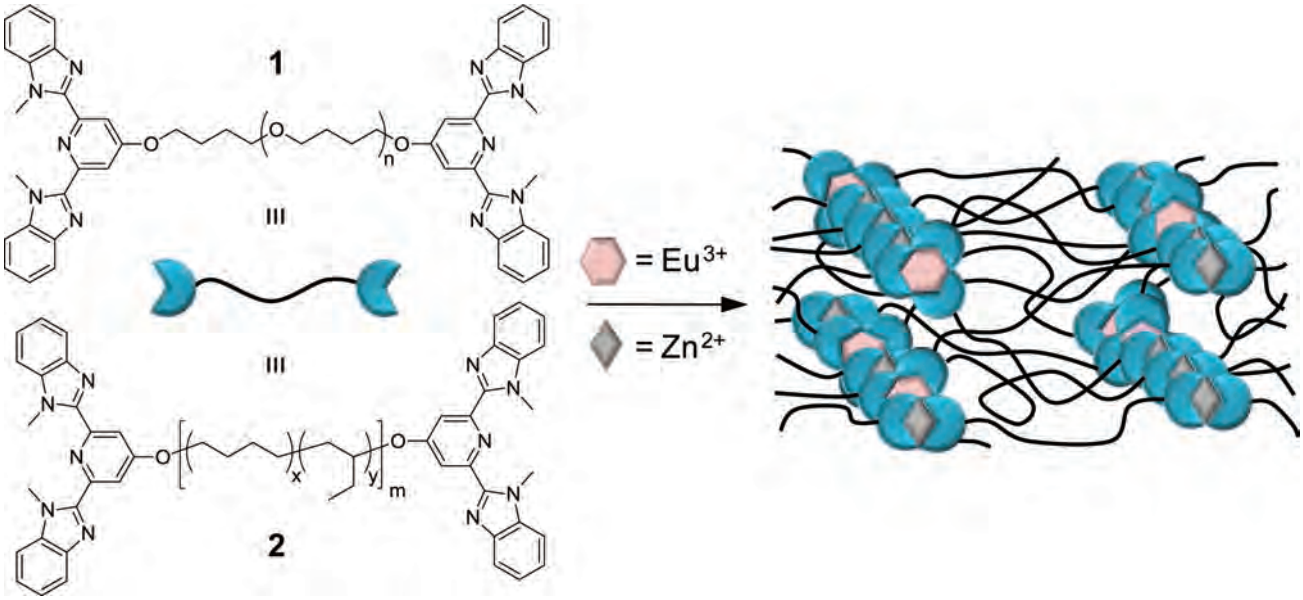
Scheme 1. Chemical Structures of Mebip End-Capped Macromonomers Studied with Poly(tetrahydrofuran) (1) and Poly(ethylene-*co*-butylene) (2) Cores[a]



[a] These macromonomers self-assemble with zinc and europium salts to yield stimuli-responsive, phase-separated network structures.

have been reported,[27−29] and similarly some of us have performed investigations into the rheological and stimuli-responsiveness of metallosupramolecular gels.[30−33] However, to date there have been no studies performed exploring the solid-state rheological properties of metallosupramolecular polymer films.

We have shown previously that elastomeric films can be prepared from ligand end-capped low-T_g polymers assembled with zinc and/or lanthanides and that these films show interesting stimuli-responsive properties that are highly dependent on the metal ion content. In particular, metallosupramolecular polymers prepared from a 2,6-bis(*N*-methylbenzimidazoyl) pyridine (MeBip) end-capped poly(tetrahydrofuran) (**1**) with zinc and europium ions yield temperature- and chemo-responsive films,[34,35] while those prepared with MeBip end-capped poly(ethylene-*co*-butylene) (**2**) yield thermo- and photo-responsive rehealable elastomers with either zinc or lanthanide ions.[36] In order to achieve a better understanding of these metallosupramolecular polymers, we report a detailed rheological study of both these materials to examine the role of the metal ions and the nature of the polymer backbone on the materials' properties.

EXPERIMENTAL METHODS

Materials Used. Compounds **1** and **2** were synthesized according to previously published methods[34−36] with molecular weights of 4200 and 4000 g/mol, respectively. All reagents and solvents were purchased from Aldrich Chemical Co. and used without further purification. Spectrophotometric grade chloroform and acetonitrile were used for all experiments.

Sample Film Preparation. Example procedure for **1** with Zn^{2+}:Eu^{3+} 70:30. 952 μL (0.01 mmol) of a $Eu(ClO_4)_3$ solution in acetonitrile (10 mM) and 1666.7 μL (0.03 mmol) of a $Zn(ClO_4)_2$ solution in acetonitrile (20 mM) were mixed with 200 mg (0.05 mmol) of **1** in 5 mL of chloroform. The solvent was removed under vacuum, and the metallosupramolecular polymer was redissolved in 2 mL of chloroform, cast into an aluminum-walled casting dish with a Teflon base, and allowed to air-dry overnight. The films were further dried in a vacuum oven at 40 °C for 6 h to remove any residual solvent before use. Films of other metal ratios were prepared by varying the amounts of $Eu(ClO_4)_3$ and $Zn(ClO_4)_2$ appropriately. Typical film thicknesses were 0.25 ± 0.05 mm.

Rheological Measurements. All experiments were carried out on a TA Instruments ARES G2 rheometer with 8 mm parallel plates. Circular disks of the films were obtained using an 8 mm diameter steel punch. Prior to each experiment, the samples were heated under compression for short periods of time (5 min, see below for more details) before cooling to 30 °C. This step is required for good adhesion between the films and the plates. It also erases any thermal history that may have resulted from crystallization of the poly(tetrahydrofuran) core of macromonomer **1**. Films of composition Zn^{2+}:Eu^{3+} 100:0 to 80:20 were heated to 130 °C under a normal force of 5 N. Films with higher europium contents required slightly lower temperatures and pressures to prevent the film from flowing out of the plates. As such, the 70:30 film was pressed at 110 °C and 5 N, the 60:40 film at 90 °C and 3 N, and the 50:50 film was pressed at 70 °C and 3 N. Strain sweeps were performed in order to determine the linear viscoelastic region for each film. Samples were strained at a constant frequency of 10 rad/s and ramped from 0.1% strain until the samples lost adhesion, which was typically at strains larger than 30%. All frequency sweep experiments were performed at 1% strain to ensure that all responses were in the viscoelastic region. Frequency sweeps were carried out over a frequency range of 0.1−100 rad/s with temperatures from 30 to 110 °C in 20 °C increments. Temperatures never exceeded 130 °C to avoid decomposition of the metal salts. The frequency sweeps for each film were then combined using time−temperature superposition to generate master curves. The reference temperature was 30 °C for all master curves.

Small-Angle X-ray Scattering (SAXS) Characterization. SAXS data were collected using a customized, pinhole collimated SAXS camera. X-rays having wavelength (λ) of 1.542 Å were generated at 45 kV and 100 mA with a Rigaku Ultrax18 rotating Cu anode and filtered using Ni foil. Two-dimensional data sets were collected using a Molecular Metrology 120 mm diameter area detector and then

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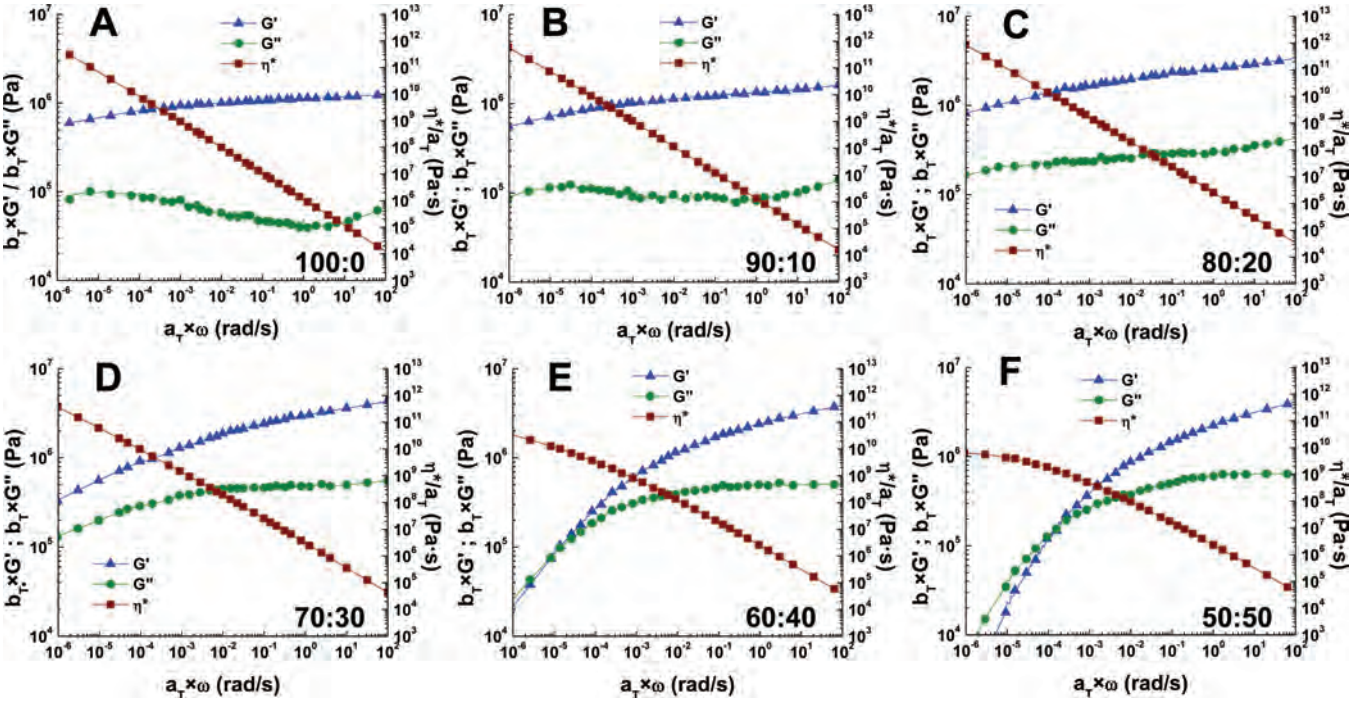

Figure 1. Master curves of films of **1** prepared with varying ratios of Zn^{2+}:Eu^{3+}. (A) 100:0, (B) 90:10, (C) 80:20, (D) 70:30, (E) 60:40, (F) 50:50. Storage modulus (triangles), loss modulus (circles), and complex viscosity (squares) vs oscillatory angular frequency. T_{ref} = 30 °C.

corrected for background noise and sample absorption. The corrected data were then azimuthally averaged to yield one-dimensional intensity, I, as a function of scattering vector magnitude, q, where $q = 4\pi \sin(\theta)/\lambda$ and 2θ is the scattering angle. The instrument was calibrated using Ag behenate, and the data were placed on an absolute scale (cm^{-1}) using type 2 glassy carbon, previously calibrated at the Advanced Photon Source, Argonne National Laboratory, as a secondary intensity standard. Each sample was characterized at two sample-to-detector distances, 150 and 50 cm, and the reduced data were combined into one continuous data set. All SAXS data processing, manipulation, and analysis were performed using Wavemetrics IGOR Pro and procedures available from Argonne National Laboratory.[37]

RESULTS AND DISCUSSION

Macromonomers **1** and **2** were prepared using methods we have previously reported.[34−36] These macromonomers were then self-assembled in solution with Zn^{2+} and Eu^{3+} perchlorate salts to yield the metallosupramolecular polymers which were then solution cast to yield elastomeric films. For mixed metal ion systems the percentages reported represent the idealized percentage of the total MeBip ligands that are coordinated with each metal ion, assuming a 2:1 Mebip:Zn^{2+} binding and a 3:1 Mebip:Eu^{3+}. For example, in a mixed Zn^{2+}:Eu^{3+} film of 70:30, 70% of the MeBip ligands can be bound to a Zn^{2+} ion and 30% of the ligand can bind to the Eu^{3+}. The metal:macromonomer ratio was calculated to ensure all ligands can bind to a metal ion and all metal ions are fully coordinated. Specifically in this study we were interested in examining the effect of two different parameters on the rheological properties of these materials, namely the effect of Zn^{2+} ions versus Eu^{3+} ions and the effect of the macromonomer core.

Influence of Eu^{3+} Content. We have previously reported,[35] using dynamic mechanical thermal analysis (DMTA), that films of the metallosupramolecular polymers of **1** with higher ratios of the Eu^{3+} to Zn^{2+} exhibit enhanced temperature sensitivity which leads to more sensitive stimuli-responsive films. Thus, to examine this effect in more detail a series of films of **1** with varying Zn^{2+}:Eu^{3+} ratios, shown in Scheme 1, were prepared ranging from 100:0 to 50:50. Metallosupramolecular polymers of **1** with less than 50% of the ligand bound to Zn^{2+} ions did not form mechanical stable films, yielding instead only oils.

The master curves obtained for the films (Figure 1) help to give insight into the structure of these metallosupramolecular polymers. From the master curves it can be concluded that there is a change in the structure as the ratio of Zn^{2+} to Eu^{3+} decreases. Films composed of 100% Zn^{2+} display typical rheological behavior of high molecular weight polymers after observation of the low-frequency region. In the case of the high Zn^{2+} content films (100:0−70:30), the terminal (flow) region cannot be reached over the range of temperatures and frequencies studied, and only the plateau region can be observed. Surprisingly, no minimum in the tan δ curve (vs ω) is observed that would correlate to a plateau modulus (see Supporting Information). Even at lower temperatures, ca. −30 °C, no minimum is found for tan δ which may result from the fact that even at −30 °C the polymer is still well above T_g of the poly(tetrahydrofuran) core (ca. −80 °C).

As the Eu^{3+} content in the films increases, the frequency at which the behavior changes from the plateau region to the terminal region shifts to higher values. This is indicative of a decrease in the effective molecular weight of the assembled macromonomers and/or a reduction of entanglements as a result of the molecular weight reduction. This gives insight into what is changing structurally as the Eu^{3+} content is increased. For a Zn^{2+}:Eu^{3+} 100:0 film, it would be expected to form a linear, high molecular weight polymer as the 2:1 Mebip:Zn^{2+} complex will just yield chain extension. Once Eu^{3+} is added, it can bind in a 3:1 Mebip:Eu^{3+} ratio which can act as a branching point. Thus, as

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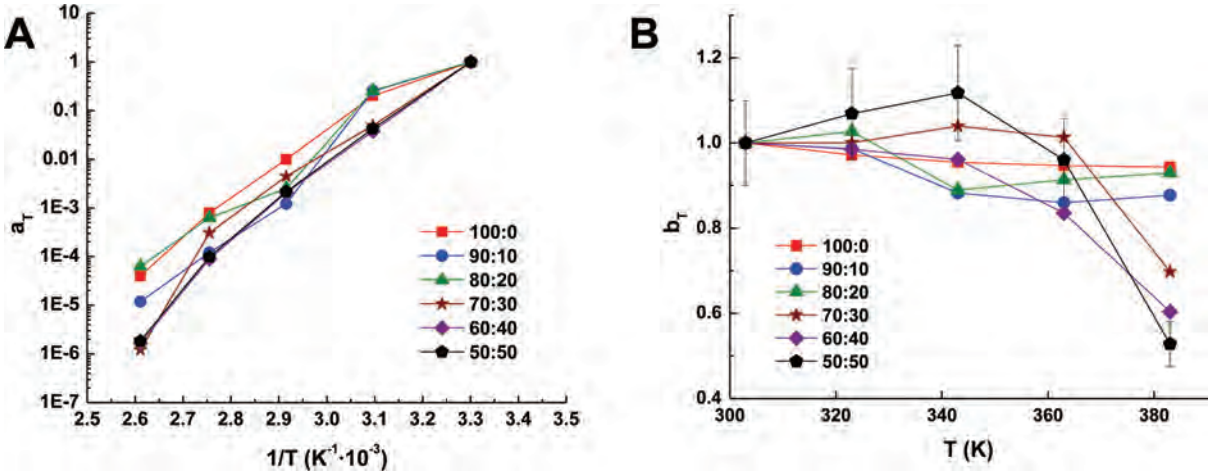

Figure 2. Horizontal (A) and vertical (B) shift factors of the series of films prepared with **1**. The difference in a_T at high temperatures suggests these films are relatively frequency dependent, whereas changes in b_T with increasing Eu^{3+} display the increased temperature sensitivity. Error bars are shown for the Zn^{2+}:Eu^{3+} 50:50 sample only for clarity; however, they apply to all of the data sets in (B). The error results from a curve fit minimizing an objective function to overlay the curves.

more Eu^{3+} is introduced, the amount of branching will increase, which will effectively reduce the molecular weight of the linear polymer segments, which are formed by chain extension with Zn^{2+} complexes between cross-links, since the amount of the Zn^{2+} is reduced, while the total molecular weight increases. Concordantly, it can be expected that the polydispersity of the linear polymer segments formed with Zn^{2+} will also increase as the Eu^{3+} content is increased, which is backed up by examination of the G'' vs ω curves. In the high content Zn^{2+} materials (100:0 and 90:10) both a minima and maxima are observed as ω is decreased in the G'' curve; however, this behavior is replaced by a more linear one as more Eu^{3+} is added, consistent with an increase in the polydispersity of the material.[38]

The relaxation time, which is roughly defined as the terminal viscosity divided by the plateau modulus, is also greatly dependent on the Eu^{3+} content within the films. It is not possible to determine the terminal viscosity for films containing 0%−30% Eu^{3+}, as the terminal region was not reached, but it is obvious that there is a trend of increasing relaxation times with decreasing Eu^{3+} content. For the films containing 40% and 50% Eu^{3+}, the terminal viscosities, which were estimated at 3.3×10^{10} and 6.3×10^{9} Pa·s, are used with estimations of the plateau modulus (3.79 and 3.97 MPa) to give relaxation times of 8700 and 1600 s, respectively. As mentioned earlier, no minimum in tan δ was observed in these films so the estimations of the plateau modulus were taken from the lowest measured tan δ value. Thus, for these two films the estimated plateau modulus is lower than the real value. The increase in the estimated plateau modulus from the 40%−50% Eu^{3+} is only 5%, which is within experimental error. Nonetheless, these results show that the relaxation times of these films are extremely dependent on the metal ratios, where a 10% increase in Eu^{3+} leads to a 5-fold decrease in relaxation time. This suggests that the decreasing terminal viscosity is primarily responsible for the dramatic decrease in relaxation times as more Eu^{3+} is added. This is likely on account of the increasing amount of Eu^{3+} increasing branching which will play a role in decreasing the viscosity. It is also possible that the decrease in terminal viscosity in the higher concentration Eu^{3+} materials is on account of the easier decomplexation of the weaker bound Eu^{3+} complexes relative to the Zn^{2+} complexes, resulting in more facile depolymerization in the system.

The effect on the temperature sensitivity with changing metal ratios can be elucidated by examining the master curve shift factors shown in Figure 2. The horizontal shift factors (Figure 2A) change in both slope and intensity which implies that these materials are quite temperature dependent. The vertical shift factors (Figure 2B) also show the dramatic change in the temperature sensitivity, particularly at high temperature, with decreasing the Zn^{2+}:Eu^{3+} ratio. For example, the shift factors for the Zn^{2+}:Eu^{3+} 100:0 film change little with temperature, while the Zn^{2+}:Eu^{3+} 50:50 film exhibits much different behavior in the temperature range studied. A trend is observed with changing metal ratio, and as the amount of Eu^{3+} is increased, the vertical shift factors move from a linear response to a larger and larger nonlinear response with temperature. This data is consistent with the previously published DMTA results[35] which show the increasing temperature sensitivity of the films with increasing amounts of Eu^{3+}.

While the temperature dependence of the vertical shift factor b_T may seem unusual, it can be explained quite simply by remembering its origin. Consider network theory[39] where the storage and loss modulus can both be written as $nk_BTf(\lambda\omega)$, where n is the number of cross-links per unit volume, k_B is Boltzmann's constant, T is temperature, and $f(\lambda\omega)$ is a function describing the modulus frequency dependence (ω) which is normalized by a relaxation time (λ). Of course, the functional form is different for the two moduli. The number of cross-links can be interpreted as the number of molecules per unit volume or entanglements per unit volume depending on model specifics for the system at hand. For linear polymer melts n can be written as $\rho N_A/M$ where ρ is the mass density, N_A is Avogadro's number, and M is molecular weight, allowing one to write the vertical shift factor as

$$b_T = \frac{[\rho N_A/M]k_BT}{[\rho_0 N_A/M_0]k_BT_0} = \frac{\rho T}{\rho_0 T_0} \quad (1)$$

where the subscript 0 is used to denote "at the reference temperature" and the molecular weight is assumed constant in

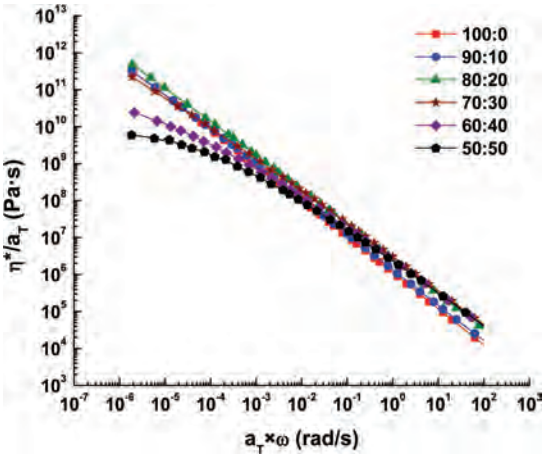

Figure 3. Time−temperature superposition plot of complex viscosity vs oscillatory angular frequency. Films of **1** with Zn^{2+}:Eu^{3+} ratios of 60:40 and 50:50 approach terminal viscosities while films containing less Eu^{3+} have nonterminal viscosities of order 10^{12} Pa·s, which is near the defined viscosity of a glass. The temperature range studied was 30−110 °C.

the later form of the equation. Since the melt density does not change very much with temperature and the absolute temperature similarly changes little, plus as temperature rises the density falls, b_T will typically change by at most 10%.

The metallosupramolecular materials studied here have a higher temperature sensitivity, especially those containing larger amounts of Eu^{3+}. This is consistent with Eu^{3+} decomplexing from the Mebip end groups as the temperature is increased. This leads to b_T falling by a factor of 2 in the case of the 50:50 material, suggesting the effective molecular weight changes with temperature. This may violate the inherent assumption of thermorheological simplicity, invalidating the use of shift factors; however, the effect is relatively mild in that the entire material does not decomplex and we believe that one can use shift factors to obtain an approximation to the full rheological response for the extended frequency range. Yet, this caveat should be kept in mind; the higher Eu^{3+} content materials may change in effective molecular weight, and the terminal region, obtained from higher temperature data, may have a smaller molecular weight than data collected at lower temperatures. Indeed, we should expect this since at higher temperatures the materials obtain low viscosity through more complete decomplexation, allowing them to heal if need be.[36]

The complex viscosity is also directly affected by the metal ion composition of the films. As the ratio of Zn^{2+}:Eu^{3+} is decreased, the viscosity is observed to decrease, most noticeably upon approaching the terminal region. As mentioned before, the transition to the terminal region is only observed for the films comprised of Zn^{2+}:Eu^{3+} 60:40 and 50:50 which can also be seen in the complex viscosity data. It is necessary to remember that the effective molecular weight for these films should be reduced as temperature is increased as a result of metal−ligand decomplexation of the more thermally responsive Eu^{3+} complexes. This suggests that the viscosity decrease is most likely a result of depolymerization at high temperatures. The probably of forming rings should also increase with increasing Eu^{3+} which may also contribute to the reduction in viscosity, although we have no evidence to directly support this idea. The film with the lowest complex viscosity (Zn^{2+}:Eu^{3+} 50:50) has a terminal viscosity of $\sim 5 \times 10^9$ Pa·s. This value is higher than any previously reported for a supramolecular polymer and may in part be related to the microphase-separated morphology of these materials (vide infra). Figure 3 shows that the complex viscosities are also shown to increase dramatically as the Eu^{3+} content is decreased as there is a 5-fold estimated increase in the terminal viscosity of the 60:40 over the 50:50 film. For films consisting of Zn^{2+}:Eu^{3+} ratios of 100:0 to 70:30, a terminal viscosity is not reached in the temperature −frequency range studied. All of these films show viscosities ranging from 5×10^{11} to 1×10^{12} Pa·s with terminal viscosities expected to be even larger. This is extremely surprising for thermoplastic elastomers, as one definition of a glass is a material exhibiting a viscosity of 1×10^{12} Pa·s.[40] These films show viscosities just below that defined transition, suggesting that these films are behaving as extremely viscous liquids.

Influence of the Core Polymer. In order to study the impact of the polymer backbone on the melt rheology behavior of these metallosupramolecular polymers, select films (Zn^{2+}:Eu^{3+} 100:0 and 50:50) were prepared from the end-capped poly(ethylene-*co*-butylene) (**2**) and compared with the previous results. Both cores have low glass transition temperatures (ca. −80 and −25 °C for **1** and **2**, respectively); however, the poly(tetrahydrofuran) core is more polar, and the oxygen atoms in the backbone have the potential to act as weak metal ion coordinating sites, which is not possible in the hydrocarbon core of **2**.

Meijer and co-workers[41] have shown that the polarity of the core polymer in telechelic supramolecular polymers assembled using hydrogen-bonding motifs influences the self-assembly process. Polar polymers were found to disrupt hydrogen bonding and dramatically reduce the mechanical properties compared to the nonpolar polymers which yielded highly phase-separated materials. Thus, it was expected in these metallosupramolecular polymers that the poly(ethylene-*co*-butylene) core would enhance the material properties of the films as it should allow for greater phase separation from the charged metal−ligand complexes, whereas the poly(tetrahydrofuran) monomer would be more miscible with the complexes and has the potential to weakly coordinate the metal ions, especially with the Eu^{3+} ions.

This anticipated difference in the microphase separation behaviors of **1** and **2** was studied using small-angle X-ray scattering (SAXS) on films of the different materials, as was recently shown for solution-cast films of **2** with Zn^{2+}.[36] Microphase-separated morphologies with appreciable long-range order give rise to constructive interference between scattered X-rays producing Bragg diffraction maxima; materials with good long-range order exhibit a higher number of Bragg maxima than those with poor long-range order. Figure 4A shows SAXS data for the series of films prepared with **1**. For all samples, two Bragg diffraction maxima are observed, characteristic of moderate long-range order. The second-order peaks are located at twice the spacing of the primary maxima (q^*), indicative of a lamellar morphology in which the poly(tetrahydrofuran) core and metal−ligand complexes form alternating layers of soft and hard phases, respectively, and consistent with those reported previously for metallosupramolecular polymers.[36] The lamellar period, d, where $d = 2\pi/q^*$, is ~8.2 nm for all samples and gives the center-to-center distance between hard phases in the case of a lamellar morphology.

When compared to the films prepared with **2**,[36] which all showed at least three Bragg diffraction maxima, it is apparent

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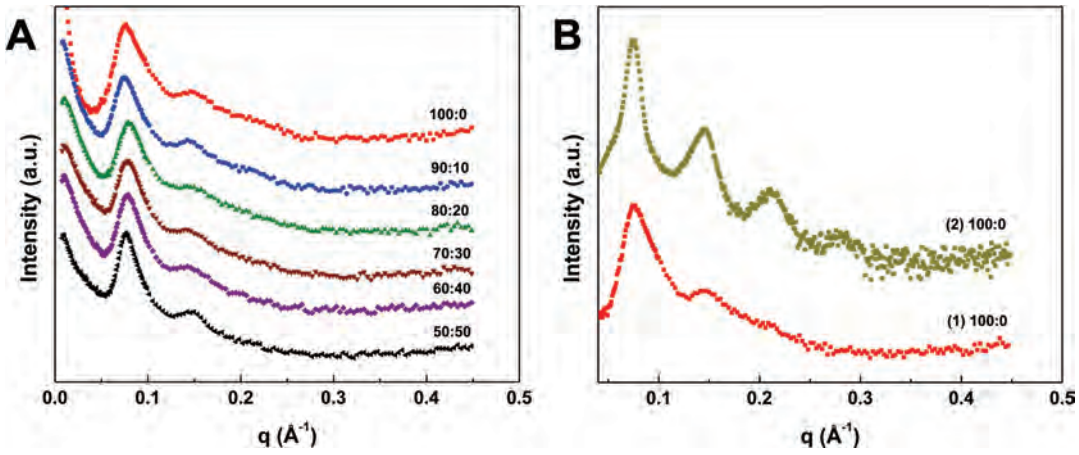

Figure 4. (A) SAXS data of films prepared with **1**. (B) Comparison of Zn^{2+}:Eu^{3+} 100:0 films prepared with **1** and **2**. Films prepared with **2** show greater long-range ordering as a result of better phase separation.

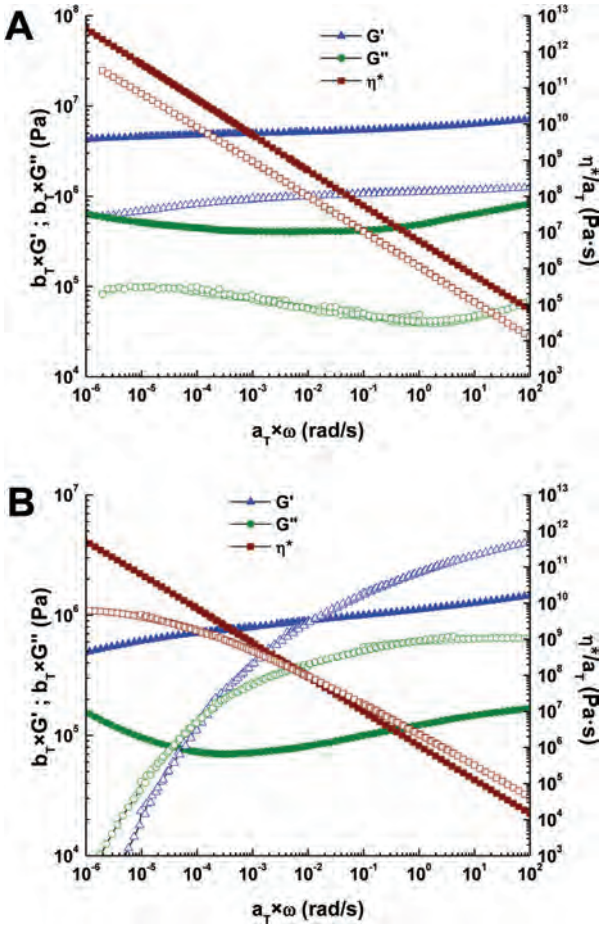

Figure 5. Direct comparison of the master curves obtained for films prepared with **1** (open) vs **2** (closed) containing various Zn^{2+}:Eu^{3+} ratios. (A) 100:0 (B) 50:50. Films prepared with **2** show enhancement in G' (triangles), G'' (circles), and η^* (squares), which is a result of better phase separation between the polymer core and metal−ligand complexes.

that the degree of ordering in the films based on **1** is significantly reduced (Figure 4B). This is consistent with the more polar poly(tetrahydrofuran) being able to interfere with the ability of the Zn^{2+} to form metal−ligand complexes with the Mebip ligand, resulting in reduced long-range order relative to the 100% Zn^{2+} sample based on poly(ethylene-*co*-butylene). Furthermore, the degree of long-range order is unaffected by the replacement of Zn^{2+} with Eu^{3+} in the materials based on poly(tetrahydrofuran). Therefore, in the case of the polar poly(tetrahydrofuran) cores, the effect of the polar core on the long-range order strongly dominates over the effect of metal ion.

As expected, the films prepared with **2** show dramatic enhancements in material properties over films prepared with **1** as shown in Figure 5. A direct comparison of the Zn^{2+}:Eu^{3+} 100:0 materials (Figure 5A) shows an order of magnitude enhancement in the modulus and viscosity just by changing the polymer core from **1** to **2**. The mechanical enhancement is most obvious when comparing the 50:50 films, focusing primarily on the lower frequency behavior. As shown earlier, films made with **1** at this metal ratio essentially displayed a terminal region, whereas films of the same metal ratio with **2** are still in the plateau region at the same frequencies and temperatures. In fact, the Zn^{2+}:Eu^{3+} 50:50 film with **2** demonstrates very similar behavior with the 100:0 film prepared with **1**, suggesting that the polymer core plays a larger role in determining the materials' properties than the two different metal ions in the mixed Zn^{2+} and Eu^{3+} films. This effect can, in part, be explained by the increased microphase separation and long-range morphology observed in the metallosupramolecular polymers of **2** when compared to **1**. As mentioned earlier, films of **1** with Zn^{2+}:Eu^{3+} 0:100 do not form stable films and result in oils. Interestingly, however, films prepared with 100% Eu^{3+} and **2** do form mechanically stable films. This is consistent with the increased phase separation imparted by the nonpolar core of macromonomer **2** and/or the ability of the poly(tetrahydrofuran) oxygens in **1** to weakly coordinate with the Eu^{3+} and compete with the ligand complexes.

Response at High Strain. Strain sweeps are generally used to determine what strain magnitude can be used in order to stay within the linear viscoelastic region which is verified as a linear response in G', G'', and tan δ. Once the stress no longer follows a linear trend, the material is said to be outside of the viscoelastic region. This can also be seen in the stress waveform which follows a sinusoidal pattern within the linear viscoelastic region while outside of this region the waveform becomes nonsinusoidal, having multiple frequency components easily visualized by a

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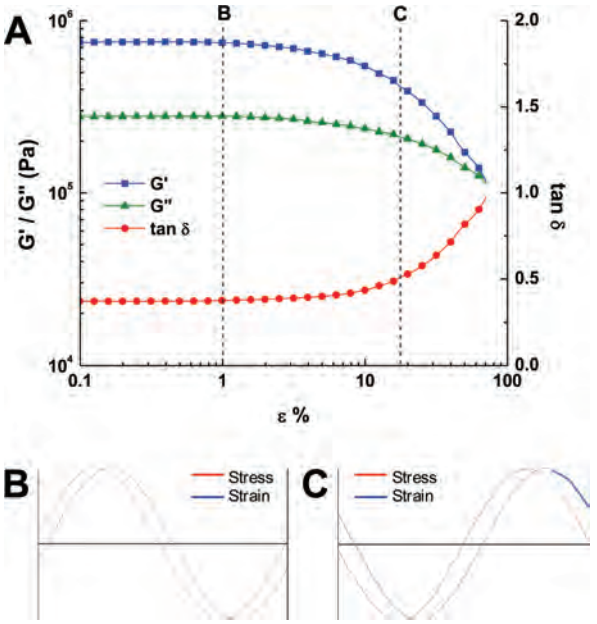

Figure 6. Strain sweep of a representative film of **1** with Zn^{2+}:Eu^{3+} 70:30. The waveform at 1% strain (B) shows a typical response in the linear region of the strain sweep. At 17.7% strain (C) the material is no longer in the viscoelastic region; however, the waveform still shows a linear response as a result of the extremely long relaxation times which prevent them from relaxing within the experiment time frame.

Fourier transform of the stress wave. Interestingly, for all Zn^{2+}:Eu^{3+} films a sinusoidal waveform is observed even though the material is no longer in the linear viscoelastic region as shown in Figure 6. The large-amplitude oscillatory strain experiments were performed with a sampling frequency of 500 data points per second, which will not influence data analysis since the frequency used in the experiments shown in Figure 6, 10 rad/s, is well below the sampling rate (as are all frequencies used in this study). Furthermore, a Fourier transform of the output torque showed no higher order harmonics, which is consistent with the model proposed below. A strain of 17.7% is well within the apparent nonlinear region as the storage modulus has decreased by a factor of ~2; however, a linear stress (torque) response is still seen. We believe this is a result of the extremely long relaxation times that are observed for these materials.

As mentioned above, the relaxation times for the two samples that displayed a terminal region were 1000−10 000 s in value. These are quite large, and because of this we do not believe the system can relax during a strain cycle. This is expected because of the phase-separated morphology prohibiting molecular motion greatly affects the destruction or creation of the network segment terms in the network theory frequently used to describe nonlinear rheological behavior.[42] The term can be written as a function of the strain or stress, which are both functions of time, exemplifying that as the strain or stress is increased, the rate of segment destruction increases and the segment creation decreases, but they are also functions of time. Here we assume the network creation rate, L, can be written as $L_0 \exp(a\gamma^0)$, where L_0 and a are constants and γ^0 is the strain amplitude, making the creation rate only a function of the strain amplitude and not time. Similarly the destruction rate, $1/\lambda$, is given by $1/\lambda_0 \exp(b\gamma^0)$, again which is dependent on the strain amplitude and not time. Of course, the strain in this experiment is given by $\gamma(t) = \gamma^0 \sin(\omega t)$, where ω is the frequency.

Since the relaxation times are so large in these materials, we hypothesize there is minimal relaxation during a strain cycle, as mentioned above, and so assume the destruction and creation rates are related to the strain amplitude. When this is done, the equations developed by Ahn and co-workers[42] are remarkably simple to solve, and the stress is a pure sinusoid of the form $\sin(\omega t + \delta)$, where δ is the phase lag, one easily finds for a singular relaxation mode

$$G' = \frac{e^{[a-b]\gamma^0}\omega^2}{e^{2b\gamma^0} + \omega^2} \quad (2)$$

$$G'' = \frac{e^{a\gamma^0}\omega}{e^{2b\gamma^0} + \omega^2} \quad (3)$$

If the material is a linear viscoelastic liquid, then a and b are zero. Note that we have written the two moduli in dimensionless form normalized by the number of network segments per unit volume, Boltzmann's constant, and temperature. It is possible to assume multiple relaxation modes and fit this nonlinear generalized Maxwell model to the data at hand. However, little is gained. Instead, we draw two conclusions from this model. First, it is possible to have a pure sinusoid in the "nonlinear" viscoelastic region. Our hypothesis is that the material cannot relax during a period of oscillation. In true polymeric materials relaxation occurs via segmental Brownian motion. Obviously, this does not occur in our materials, and structural recovery is slow and related to the materials' morphology, the metal ions coordinating with the end groups and in the case of **1** with the oxygen atoms present in the polymeric backbone. The thermal energy is obviously insufficient to allow rapid recovery for the conditions we have chosen to use.

Second, eqs 2 and 3 are extremely robust in their predictions. The relative magnitude of a and b can change the strain response of the material to generate rheological phase diagrams suggested by Ahn and co-workers. The results in Figure 6 suggest $a > b$ since both G' and G'' decrease with γ^0. Of course, detailed modeling would be required to satisfactorily fit the moduli data over all frequencies and strains.

As stated above, we would learn little in performing this exercise since arbitrary assumptions would have to be made. For example, many relaxation modes are required to fit the data over the entire frequency range. Would only the first mode be represented by eqs 2 and 3, or would all modes? Would the network creation and destruction parameters a and b be different for each mode? Either or both of these assumptions could generate satisfactory data representations, and so we do not do so. This model is very powerful though and rich in its predictions and lends credence to our hypothesis that relaxation during a deformation cycle does not occur.

As far as we know, this is the first observation of this effect where a pure sinusoid is observed in the so-called nonlinear region. The materials synthesized in this work are obviously unusual when compared to conventional covalent polymers; however, we do not believe that this effect is unique. If another system cannot relax during an oscillation period, then similar behavior could be observed. Obviously, our system has extremely large relaxation times, allowing us to demonstrate this behavior.

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CONCLUSIONS

A detailed study of the rheological behavior of a series of metallosupramolecular films in the melt was carried out to determine the impact of changing metals and the macromonomers. It was found that in films with varying ratios of zinc and europium increasing the europium content resulted in a dramatic change in the temperature response which allowed the films to reach the terminal region. It was also determined that the polymeric core plays a significant role in the materials' properties where a nonpolar poly(ethylene-*co*-butylene) core displayed dramatic enhancement of G', G'', and η^* relative to the more polar poly(tetrahydrofuran) core. All of the films studied had terminal complex viscosities greater than 1×10^9 Pa·s, which is higher than any previously reported for a supramolecular polymer and near to the value that defines a glass (1×10^{12} Pa·s). The films exhibited a sinusoidal waveform in the "nonlinear" viscoelastic region of the strain sweeps as a result of extremely long relaxation times which prevents the material from relaxing during a period of oscillation. We used this to develop a simplified network model which can be applied to other materials that are unable to relax during an oscillation period.

ASSOCIATED CONTENT

Supporting Information. Master curves of Zn^{2+}:Eu^{3+} 0:100 with **1** and **2**; tan δ curves of films with **1**; strain sweeps of films with **1**; shift factors of films with **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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